

Electron Ionization Mass Spectrometric Studies of Homalicine tetraacetate, Dihydrohomalicine tetraacetate and Related Compounds

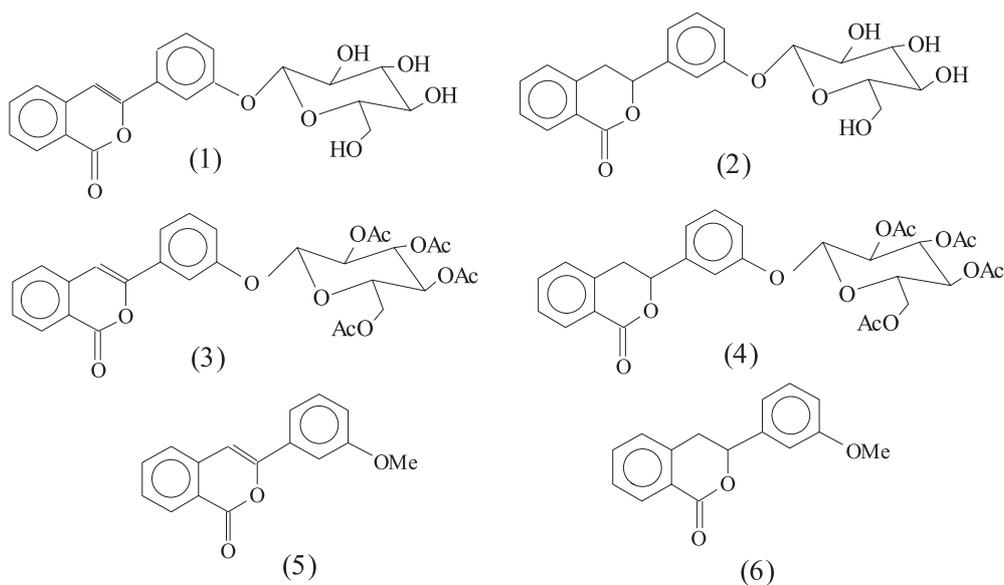
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Electron Ionization mass spectra of homalicine tetraacetate (**3**), dihydrohomalicine tetraacetate (**4**) and related compounds (**5,6**) are described with the help of EIMS. The molecular formulae are further confirmed by HREIMS peak matching of molecular ion peaks exhibited by EIMS.

Introduction

Homalicine (**1**) and dihydrohomalicine (**2**) were isolated¹ from acetone extract of the roots of *Homalium zeylanicum* Benth. We have already reepported² the total synthesis of these natural products. Here we report electron ionization mass spectrometric



(EIMS) studies of homalicine tetraacetate (**3**), Dihydrohomalicine tetraacetate (**4**), 3-(3'-methoxyphenyl)isocoumarin (**5**) and 3-(3'-methoxyphenyl)-3,4-dihydroisocoumarin (**6**). The molecular formulae of

the compounds (**3-6**) have been confirmed by high resolution electron ionization mass spectral (HREIMS) peak matching of molecular ion peaks exhibited by EIMS, as shown in the Table.

Table HREIMS of Molecular Ion Peaks of Compounds (**3-6**)

Compound Mol.	Formulae	M ⁺ (m/z)	
		Calculated	Found
3	C ₂₉ H ₂₈ O ₁₂	568.15807	568.15814
4	C ₂₉ H ₃₀ O ₁₂	570.1737	570.1740
5	C ₁₆ H ₁₂ O ₃	252.0786	250.0804
6	C ₁₆ H ₁₄ O ₃	254.0943	254.0955

Results and Discussion

The general fragmentation patterns of these compounds are assigned with the help of low resolution electron ionization mass spectra (LREIMS) as depicted in schemes 1-4.

Homalicine tetraacetate (**3**)

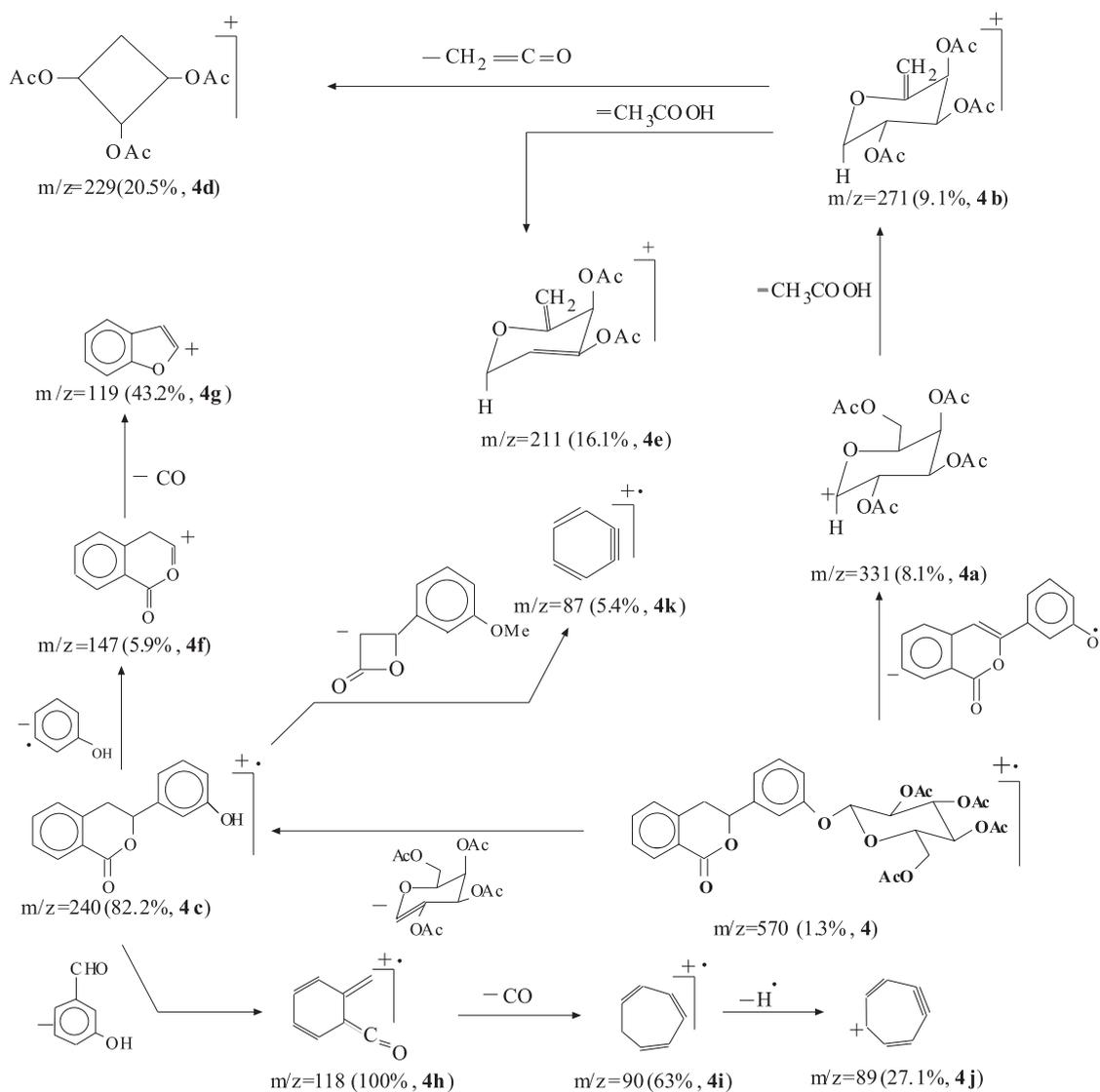
The EIMS of (**3**) exhibited a molecular ion at m/z 568 (C₂₉H₂₈O₁₂, **3**), which afforded a radical cation at m/z 238 (C₁₅H₁₀O₃, **3c**) by the loss of acetylated glucose moiety. The loss of 3-(3'-oxophenyl)isocoumarin radical from (**3**) afforded an acetylated glucose cation at m/z 331 (C₁₄H₁₉O₉, **3a**). The removal of a hydroxal radical and a ketene radical from (**3c**) yielded cations at m/z 121 (C₇H₅O₂, **3h**) and m/z 221 (C₁₅H₉O₂, **3e**) respectively, followed by the removal of a CO molecule from (**3e**) to afford a cation m/z 193 (C₁₄H₉O, **3i**). The loss of a phenol radical and a CO molecule from (**3c**) gave a cation at m/z 145 (C₉H₅O₂, **3j**) and a radical cation at m/z 210 (C₁₄H₁₀O₂, **3f**) respectively. The removal of a CO molecule from (**3j**) and a phenol radical from (**3f**) yielded a cation at m/z 117 (C₈H₅O, **3k**). The cation at m/z 271 (C₁₂H₁₅O₇, **3b**) was formed from (**3a**) by the loss of an acetic acid molecule which produced actions at m/z 229 (C₁₂H₁₃O₆, **3**) and 211 (C₁₀H₁₁O₅, **3g**) by the evolution of ketene and CH₃COOH molecules respectively, as depicted in Scheme 1.

Dihydrohomalicine tetraacetate (**4**)

EIMS of (**4**) afforded a molecular ion at m/z 570 (C₂₉H₃₀O₁₂, **4**). The fragmentation pattern of this radical cation is shown in Scheme 2.

3-(3'-Methoxyphenyl)isocoumarin (**5**)

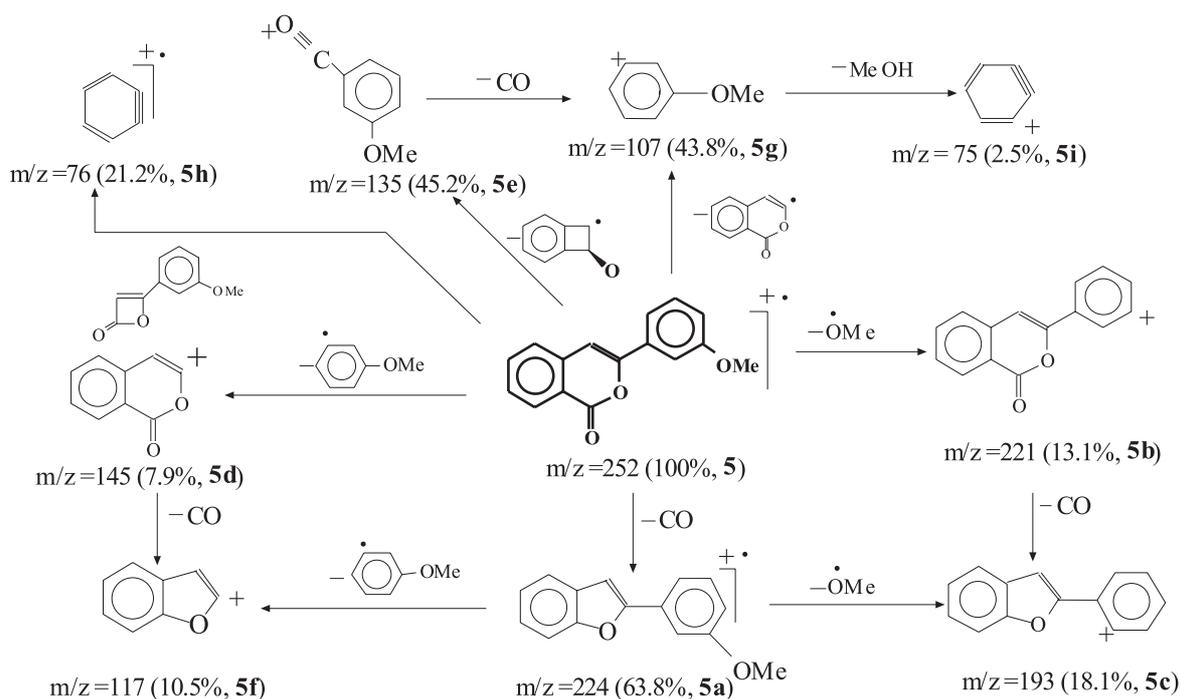
A molecular ion at m/z 252 (C₁₆H₁₂O₃, **5**) was obtained by the EIMS of (**5**). The fragmentation pattern of this radical cation is shown in scheme 3.



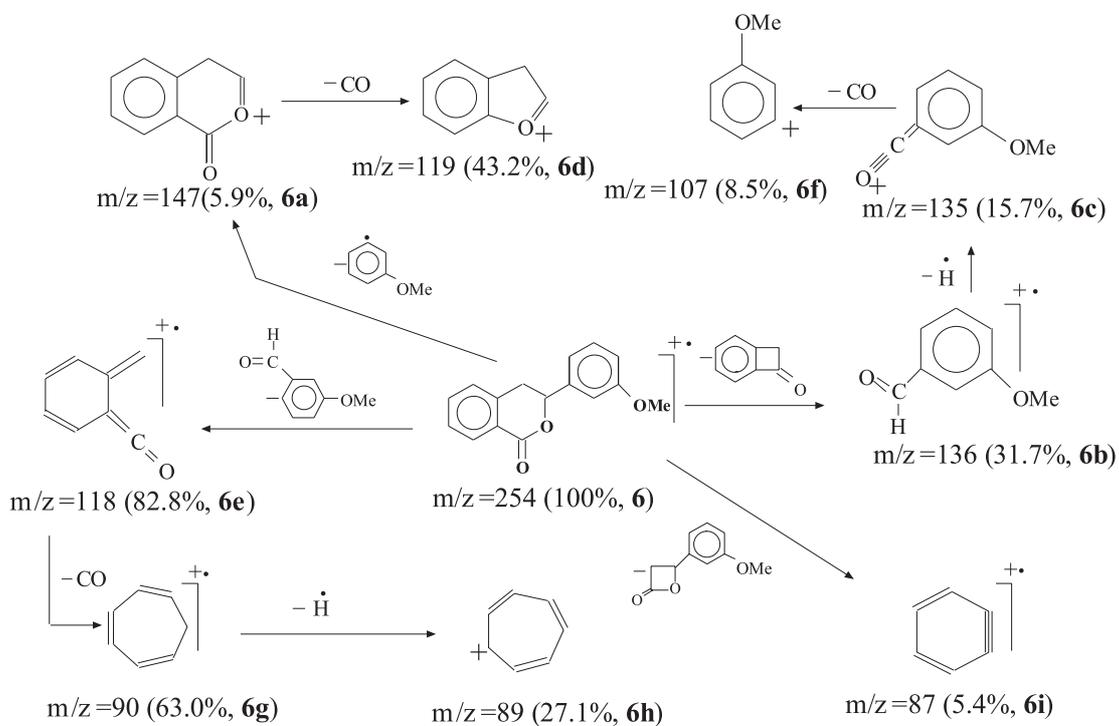
Scheme 2

3 – (3'-Methoxyphenyl)-3,4-dihydroisocoumarin (6)

A molecular ion at m/z 254 ($\text{C}_{16}\text{H}_{14}\text{O}_3$, **6**) was obtained by the EIMS of (**6**). The fragmentation pattern of this radical cation is shown in scheme 4.



Scheme 3



Scheme 4

Experimental

Compounds (**1-6**) were prepared according to literature³ procedures. All of these compounds were characterized by IR, mass, ¹³C-NMR and ¹H-NMR spectral data and elemental analysis. The EIMS were recorded on a MAT-311 instrument with an accelerating voltage of 3kV and ionization energy of 70eV. The temperature of the ion source was maintained at 250°C.

References

1. T. R. Govindachari, P. C. Parthasarathy, H. K. Desai and K. S. Ramachandran, **Indian J. Chem.**, **13**, 537-40 (1975).
2. M. T. Hussain, N. H. Rama and A. Malik, **Helv. Chim. Acta**, (2000) (submitted)
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